This invention relates to a method for preventing the increase in concentration of inorganic chloride salts in a molten nitrate-nitrite salt quench bath beyond a tolerable limit. More in particular this invention relates to a method of economically removing excess inorganic chloride salts from an inorganic molten nitrate-nitrite salt bath, used for quenching of steel articles, commonly referred to as austempering or martempering.

In one process of austempering a steel article, the article is immersed in an austenitizing bath of molten alkali metal chlorides at about 1600°F. for a specified period of time. A commonly used commercial chloride austenitizing bath for such purpose may consist of a mixture containing about 50% sodium chloride and about 50% potassium chloride. After the immersion time of the article in the fused chloride mixture has elapsed, the article is removed from the chloride austenitizing bath and immediately immersed in an austempering quench bath. The austempering quench bath initially may consist of a mixture of about 20% sodium nitrate, 52% potassium nitrate, and about 28% sodium nitrite maintained at a temperature of about 750°F. After immersion in the austempering quench bath for a specified period of time the article is removed, cooled and rinsed free of adhering salts. Further treatment of the article is according to conventional methods which form no part of the present invention and will therefore not be further considered.

When the article is transferred from the chloride austenitizing bath to the austempering quench bath, some of the chloride salts physically adhere to the article, are deposited in the quench bath when the article is immersed therein, and go into solution. From this it can be appreciated that with repeated austempering operations with successive steel articles in the same baths, the concentration of chloride salts in the quench bath gradually increases. Since the melting point of the initial nitrate-nitrite quench bath is in the order of about 300°F, while that of the chlorides is about 1300°F, the chloride content of the quench bath will increase until it reaches its limit of solubility in the nitrate-nitrite bath, after which additional chlorides will precipitate out and settle to the bottom of the bath or will freeze against colder surfaces within the bath. As it is desirable to maintain the quench bath at about 750°F, it becomes obvious that the bath will become contaminated to the point where it will be completely unusable and could even freeze at this temperature if the chloride content becomes sufficiently high. It has been found that the quench bath at 750°F can tolerate the presence of chloride salts up to about 17% by weight at maximum concentration. Thus if the chloride content exceeds about 17% by weight, the chlorides precipitate out, forming a sludge in the quench bath. At this point the quench salts are either (1) completely or partly discarded and replaced by fresh nitrate-nitrite salts or (2) the sludge is manually bailed out by means of a screened shovel which allows the nitrate-nitrite salts to pass through but retains the precipitated chlorides. Because of wetting action, the sludge which is discarded may contain up to 70% nitrate-nitrite salts and only 30% chloride salts. However, such procedure is not desirable because sodium nitrate, potassium nitrate and sodium nitrite salts are much more expensive than the chloride salts which are comparatively cheap. Thus the problem is to remove the chloride salts from the quench bath with minimal loss of nitrate-nitrite salts for maintaining fused condition of the quench bath at its operating temperature, thereby reducing the cost of the austempering operation.

It is therefore an object of this invention to separate inorganic alkali metal chlorides from a molten alkali nitrate-nitrite salt quench bath.

A further object of this invention is to recover economically a major portion of the sodium nitrate-potassium nitrate-nitrite salts from an austempering and martempering quench bath for re-use in said bath.

Another object of this invention is to reclaim economically the sodium nitrate-potassium nitrate-nitrite salts of an austempering and martempering quench bath for re-use in said bath by removing the major portion of chloride salts therefore.

Another object of this invention is to economically remove sufficient chloride salts from an austempering and martempering quench bath to maintain the freezing temperature of said bath substantially below its desired operating temperature.

Another object is to maintain the chloride content of the quench bath both low and constant so that the quenching power of the bath is stabilized at an efficient nitrate-nitrite composition.

These and other desirable and important objects inherent in and encompassed by the invention will be more readily understood from the ensuing description, the appended claims and the annexed drawings wherein:

Figure 1 is a diagram illustrating schematically the components comprising the apparatus and their respective relationship to the invention.

Figure 2 is a diagram illustrating schematically the components comprising the apparatus and their respective relationship to each other in a modified form of the invention.

As mentioned previously in repeated austempering and martempering operations, by mechanical adherence to the articles being austenitized in the alkali metal chloride bath (not shown) chloride salts are mechanically deposited in the austempering and martempering quench bath 10 (Figure 1), and after a time the build-up of chloride salt content in the bath 10 would reach a concentration such that the bath 10 would no longer remain fluid at the desired quenching temperature. When the chloride content exceeds its solubility at the operating temperature of the bath, freezing begins on the walls of the receptacle 11 supporting the bath 10 and progresses inwardly until the bath is completely sludge over, and/or the excess chlorides are precipitated within the bath 10 and settle to the bottom of the tank until the bath is completely inoperable for its intended purpose. This can be avoided as follows:

Referring to Figure 1 there is provided a plate separator 12 communicatively connected to the bath 10 by a pipe indicated at 13 on the upper portion thereof. The lower portion of the bath 10 is communicatively connected to the outer side of a pump 14 by a pipe indicated at 14. The inlet side of the pump P is communicatively connected to the pot 12 by the pipe indicated at 15. Thus the pump P functions to circulate the liquid salts of the bath 10 through the pot 12. The temperature in pot 12 is maintained at or above the operating temperature of bath 10. The pot 12 is provided with a removable separator plate 16 partly immersed therein. The plate 16 is provided with conventional passages (not shown) for circulating a fluid coolant therethrough.
liquid coolant enters the plate 16 at the inlet ports 17 and 17' and is discharged through the outlet ports 18 and 18' as shown in Figure 1. In order to prevent a appreciable temperature reduction of the pot 12 it is preferred that the coolant be adjusted to maintain the plate 16 at about 100° F. below the temperature of pot 12. Thus the plate 16 being about 100° F. cooler than the pot 12 causes the chloride salts to adhere and crystallize back on the plate 16. When the plate 16 contains an appreciable amount of adhered chloride salts the entire plate 16 is mechanically removed from the pot 12 and partly immersed (to the same extent as that in the pot 12) into a low temperature or quench pot 19 as indicated schematically by the arrow 20. For convenience when the plate 16 is removed from the separator pot 12 to the low temperature or quench pot 19 it is referred to by the numeral 16'.

The quench pot 19 contains a liquid solution 22 of about 87% by weight of nitrate-nitrite salts with about 10% water and up to about 3% chloride salts. With reference to chloride salts (potassium chloride and sodium chloride) this composition at 3% chloride salt corresponds to the maximum solubility of the chloride salts in such a bath. The quench pot 19 is maintained at a temperature of between 275° F. and 325° F., preferably at about 300° F. In order to provide water to form with the adhered solution a mixture which will control the temperature in the quench pot 19 a water inlet pipe 21 is provided which may or may not extend below the surface of the liquid in the quench pot 19. The water entering the pipe 21 may conveniently be the rinse water obtained when rinsing the quenched articles. Hence, its solution at about 3% as well as chlorides. Thus the nitrate-nitrite salts may be recovered in a simultaneous operation.

When the plate 16 is mechanically removed from the pot 12 the salts adhered thereto consists of a sludge containing about 60% chloride salts in solid form and the remainder is essentially liquid nitrate-nitrite salts mechanically occluded with the solid chlorides. As soon as the plate 16 is immersed as 16' in the quench pot 19, the sludge loses its adherence to the plate 16' apparently due to the temperature gradient between the plate 16' and solution 22 and the increased solubility of the nitrate-nitrite salts in solution 22 because of the water therein. The chlorides precipitate while solution 22 is maintained essentially unchanged by adding water to keep an amount of about 10% water in the bath. Although the chloride precipitate in the quench pot 19 is indicated as settling on the bottom as indicated at 23, what really takes place is that a slurry is formed in the quench pot wherein the liquid phase is solution 22 and the solid phase is a mixture of potassium chloride and sodium chloride. Thus the slurry comprise the solution 22 and the precipitated chloride salts 23. The slurry 22, 23 is drawn from the quench pot 19 into a mechanical separator 24 through the communicating pipe 25 which may be by gravity or a pump (not shown) interposed in the pipe 25. The mechanical separator 24 may comprise a conventional unit such as a filter press or centrifuge. The solids removed by the separator 24 are deposited into the discharge 26 through the pipe 27 and comprise mainly chloride salts with whatever small amount of solution 22 which may adhere after mechanical separation and subsequent rinsing processes. The remainder of the solution 22, containing about 87% by weight of nitrate-nitrite salts, 10% water and about 3% chloride salts, discharged from the mechanical separator 24 is deposed either directly or after being reheated to remove the water in the austempering quench bath 10 through the pipe 28 by means of gravity or a pump (not shown) interposed therein. It also could be cast into bars, allowed to freeze, and then added to the bath 10.

Replenishment of the solution 22 in the quench pot 19 is from the water introduced through the pipe 21, and the nitrate-nitrite salts occluded in the adhered chloride salts cast into bars in order to prevent a 10% water reduction in the quench pot 12 to the quench pot 19 on the separator plate 16 and 16'. As pointed out previously the salt deposit on the plate 16 consists of about 60% chloride salts and about 40% mechanically occluded liquid nitrate-nitrite salts. The salts delivered to the receiver 26 containing mostly chlorides and the balance nitrate-nitrite salts are discarded if it is not practical from an economical point of view to subject this material to a further extraction process.

From the above it has been shown a practical and economical method of reclaiming in excess of 80% of the nitrate-nitrite salts which can be effectively re-cycled back to the austempering quench bath 10.

Figure 2 shows a modified form of the invention wherein the separator plate 16 and 16' and the plate separator pot 12 are eliminated and yet comparable results can be obtained with that described previously. For clarity the components employed in the modified form of the invention which are similar to that of Figure 1 are designated by like numerals except that each is increased by 100. Thus the alkali nitrate-nitrite salt quench bath 110 is formed by walls 111. The fused salts of the bath 110 flow directly into the low temperature pot 10 which also serves to control the temperature in the quench pot 19 a water inlet pipe 21 is provided which may or may not extend below the surface of the liquid in the quench pot 19. The water entering the pipe 21 may conveniently be the rinse water obtained when rinsing the quenched articles. Hence, its solution at about 3% as well as chlorides. Thus the nitrate-nitrite salts may be recovered in a simultaneous operation.

When the plate 16 is mechanically removed from the pot 12 the salts adhered thereto consists of a sludge containing about 60% chloride salts in solid form and the remainder is essentially liquid nitrate-nitrite salts mechanically occluded with the solid chlorides. As soon as the plate 16 is immersed as 16' in the quench pot 19, the sludge loses its adherence to the plate 16' apparently due to the temperature gradient between the plate 16' and solution 22 and the increased solubility of the nitrate-nitrite salts in solution 22 because of the water therein. The chlorides precipitate while solution 22 is maintained essentially unchanged by adding water to keep an amount of about 10% water in the bath. Although the chloride precipitate in the quench pot 19 is indicated as settling on the bottom as indicated at 23, what really takes place is that a slurry is formed in the quench pot wherein the liquid phase is solution 22 and the solid phase is a mixture of potassium chloride and sodium chloride. Thus the slurry comprise the solution 22 and the precipitated chloride salts 23. The slurry 22, 23 is drawn from the quench pot 19 into a mechanical separator 24 through the communicating pipe 25 which may be by gravity or a pump (not shown) interposed in the pipe 25. The mechanical separator 24 may comprise a conventional unit such as a filter press or centrifuge. The solids removed by the separator 24 are deposited into the discharge 26 through the pipe 27 and comprise mainly chloride salts with whatever small amount of solution 22 which may adhere after mechanical separation and subsequent rinsing processes. The remainder of the solution 22, containing about 87% by weight of nitrate-nitrite salts, 10% water and about 3% chloride salts, discharged from the mechanical separator 24 is deposed either directly or after being reheated to remove the water in the austempering quench bath 10 through the pipe 28 by means of gravity or a pump (not shown) interposed therein. It also could be cast into bars, allowed to freeze, and then added to the bath 10.
What is claimed:

1. For reducing contaminating excess alkali metal chlorides content of a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of flowing said contaminated molten bath into a low temperature pot, introducing into said pot up to about 10% by weight of water to form a liquid solution with said salts for precipitating excess alkali metal chlorides in solid phase, and mechanically separating said solid phase alkali metal chlorides from said liquid composition.

2. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of transferring at least a portion of said contaminated molten bath into a low temperature pot, introducing into said pot up to about 10% by weight of water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition, and discharging said liquid phase composition into said bath.

3. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of transferring at least a portion of said contaminated bath into a low temperature pot, adding to said pot sufficient water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition and discharging said liquid phase composition into said bath.

4. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing salts selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method of transferring at least a portion of said contaminated bath into a low temperature pot, said pot being maintained at a temperature between about 257° F. and about 325° F., introducing into said pot sufficient water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition and discharging said liquid phase composition into said bath.

5. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of sodium nitrate, potassium nitrate, and sodium nitrite, the method of transferring at least a portion of said contaminated bath into a temperature between about 257° F. and about 325° F., introducing into said pot sufficient water to form a liquid phase composition with said salts for precipitating excess alkali metal chlorides and the balance being said nitrogen containing salts for precipitating alkali metal chlorides in excess of said 3% by weight in solid phase, mechanically separating said solid phase alkali metal chlorides substantially from said liquid phase composition and discharging said liquid phase composition into said bath.

6. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method comprising the flowing of said contaminated molten bath into a separator pot, providing a plate, means for maintaining the temperature of said plate substantially below the temperature of said bath, providing a plate, means for maintaining the temperature of said plate having a liquid solution comprising of up to about 3% by weight alkali metal chlorides with water and at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, said liquid solution being maintained at a temperature substantially below the temperature of said plate, immersing at least a portion of said plate into said separator pot for inducing at least a portion of said chlorides of said bath to precipitate in solid phase on said plate, mechanically removing from said separator pot, said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said plate with said solid phase chlorides into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid phase chlorides from said liquid solution and returning said extracted liquid solution to said austempering and martempering quench bath.

7. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method comprising the transferring of said contaminated molten bath into a separator pot, providing a plate, means for maintaining the temperature of said plate approximately 100° F. below the temperature of said separator pot, providing a liquid phase pot, said low temperature pot having a liquid solution comprising of up to about 3% by weight of alkali metal chlorides with about 10% by weight of solid water and the balance being at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, said liquid solution being maintained at a temperature of about 275° F., to about 325° F., immersing at least a portion of said plate in said separator pot for inducing at least a portion of said chlorides of said bath to precipitate in solid phase on said plate, mechanically removing said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said plate with said solid phase chlorides into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid phase chlorides from said liquid solution and returning said extracted liquid solution to said austempering and martempering bath.

8. For removing substantially all contaminating alkali metal chlorides in excess of about 3% by weight from a molten austempering and martempering quench bath initially containing at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, the method comprising the transferring of at least a portion of said contaminated bath into a separator pot, providing a plate, means for maintaining the temperature of said plate approximately 100° F. below the temperature of said separator pot, providing a low temperature pot, said low temperature pot containing a liquid solution comprising of up to about 3% by weight of alkali metal chlorides with water and the balance being at least one salt selected from the group consisting of alkali metal nitrates and alkali metal nitrites, means for introducing into and maintaining about 10% by weight of water in said liquid solution, said liquid solution being maintained at a temperature of about 275° F., to about 325° F., immersing at least a portion of said plate in said separator pot for inducing at least a part of said chlorides of said bath to precipitate in solid phase on said plate, mechanically removing said plate with said precipitated chlorides adhered there-
plate with said solid phase chlorides into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid chlorides substantially from said liquid solution and returning said extracted liquid solution to said austempering and marquenching bath.

9. For removing substantially all contaminating alkali metal chloride salts in excess of about 3 percent by weight from a molten austempering and marquenching quench bath initially containing at least one salt selected from the group consisting of sodium nitrate, potassium nitrate, and sodium nitrite, the method comprising the transferring of at least a portion of said contaminated bath into a separator pot, providing a plate, means for maintaining the temperature of said plate at approximately 100° F., below the temperature of said pot, providing a low temperature pot, said low temperature pot containing a liquid solution comprising of up to about 3% by weight of alkali metal chlorides with water and the balance being at least one salt selected from the group consisting of sodium nitrate, potassium nitrate, and sodium nitrite, means for introducing into and maintaining about 10 percent by weight of water in said liquid solution, said liquid solution being maintained at a temperature of about 275° F., to about 325° F., immersing at least a portion of said plate in said separator pot for inducing at least a part of said chloride of said bath in excess of about 3 percent by weight to precipitate in solid phase on said plate, mechanically removing said plate with said precipitated chlorides adhered thereto and thereafter immersing at least a portion of said plate with said solid phase chloride salts into said liquid solution in said low temperature pot for depositing said solid phase chlorides therein, mechanically extracting said solid chlorides substantially from said liquid solution and returning said extracted liquid solution to said austempering and marquenching bath.

No references cited.